1. Introduction

Light olefins, especially propylene, are important starting materials for many chemical processes, so demand continues to rise every year. Light olefins provide very versatile building blocks for synthesis and are the feedstocks for a wide range of important monomers, polymers, intermediates and chemicals. Primary production of light olefins is based on either steam cracking or recovery from refinery processes. However, methanol can be easily obtained from the huge reserves of natural gas, so the methanol-to-olefin (MTO) reaction has gained interest recently.

Many researchers have concentrated on converting methanol to hydrocarbons such as methanol to gasoline (MTG), methanol to hydrocarbons (MTH) and MTO using zeolitic catalysts such as ZSM-5(1)−(3), zeolite Beta(4,5), and SAPO-34(6−8), and the reaction paths of MTO and MTG processes over zeolitic catalysts have been reported(9). Silicoaluminophosphate SAPO-34 (pore size ca. 0.43 nm) is an excellent catalyst for the selective production of light olefins (ethylene and propylene) in the MTO reaction. However, this catalyst is rapidly deactivated by coke accumulation in the internal narrow channels of SAPO-34 crystals(10,11).

H-ZSM-5 zeolite was treated with phosphorus acid by impregnating H-ZSM-5 with aqueous solutions of phosphoric acid at various concentrations. H-ZSM-5 (P-HZSM-5) modified with phosphoric acid was used as a catalyst for the methanol-to-olefin reaction. The molar ratios of P/Si and Si/Al in H-ZSM-5 and P-HZSM-5 were measured by EDX analysis. The Si/Al molar ratios of P-HZSM-5 increased with higher concentration of H3PO4 in the solution, which might be caused by partial dealumination of H-ZSM-5 by the H3PO4 treatment. The P/Si molar ratio of P-HZSM-5 after washing was proportional to the H3PO4 concentrations in the aqueous solutions. The remaining phosphorus species after the washing must be strongly adsorbed by interaction with the pore surface of H-ZSM-5 zeolite. The P-HZSM-5 catalyst showed very high propylene selectivity up to 57% with methanol conversion of 100%. Furthermore, catalyst stability was significantly improved for the P-HZSM-5 catalysts. Ammonia TPD spectra showed that the strong acid sites of H-ZSM-5 disappeared after the phosphoric acid treatment. Consequently, the formation of aromatics and coke was inhibited, resulting in higher light olefin selectivity and catalyst stability.

2. Experimental

2.1. Catalyst Preparation and Characterization

H-ZSM-5 (Tosoh Corp., crystal size = ca. 3 μm, SiO2/Al2O3 = 310 (EDX analysis)) was used as the cat-

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H-ZSM-5 was impregnated with phosphoric acid (H$_3$PO$_4$) aqueous solutions of various concentrations. First, 1.00 g H-ZSM-5 was mixed with 5.00 g of deionized water, then the appropriate amount of 85 wt% H$_3$PO$_4$ was added. The amounts of 85 wt% H$_3$PO$_4$ added and the concentrations of the H$_3$PO$_4$ aqueous solutions are listed in Table 1. The solvents were completely evaporated by heating. Therefore, all H$_3$PO$_4$ molecules in the solutions were loaded on the H-ZSM-5. The mass ratios of phosphorus (P) in the solutions to H-ZSM-5 were 0.01, 0.02, 0.03, 0.045 and 0.055. The H-ZSM-5 samples modified with H$_3$PO$_4$ (P-HZSM-5) were designated as: 1P-Z, 2P-Z, 3P-Z, 4.5P-Z and 5.5P-Z, respectively. The P-HZSM-5 catalysts were dried again at 383 K for 5 h and then calcined in air at 873 K for 5 h with a heating rate of 1 K/min. After calcination, the samples of 1P-Z, 2P-Z, 3P-Z, 4.5P-Z and 5.5P-Z were washed with deionized water to remove excess H$_3$PO$_4$ on the catalysts. Here, the P-HZSM-5 samples were immersed in deionized water for 3 h at room temperature with stirring, then dried at 383 K and calcined again at 873 K for 5 h. After washing, the samples were renamed W1P-Z, W2P-Z, W3P-Z, W4.5P-Z and W5.5P-Z.

The products were characterized by X-ray diffraction (XRD) using a Rigaku Miniflex with Cu-Kα radiation. The chemical compositions of the samples were analyzed by Energy Dispersive X-ray Spectrometry (EDX). The acidic strength of the samples was analyzed by temperature-programmed desorption of ammonia (NH$_3$-TPD) using an Autosorb-1-Chemi (Quantachrome Instruments) in the temperature range from 373 to 973 K. A 0.2 g sample was pretreated in helium at 773 K for 1 h, then cooled to 373 K for 1 h. After NH$_3$ was adsorbed on the samples for 2 h, temperature-programmed desorption was started at 10 K/min from 373 to 973 K using a Quantachrome TPRWin v2.0.

### 2.2 Catalytic Test

MTO reactions over H-ZSM-5 and P-HZSM-5 catalysts were performed using a fixed bed reactor made of quartz glass (i.d. 4 mm) with a continuous flow system under atmospheric pressure. The temperature and W/F (mass of the catalyst [kg] divided by the feed rate of methanol [mol/h]) were systematically varied for comparison. The reaction products were analyzed by a GC-14B (Shimadzu Corp.) gas chromatograph equipped with a flame ionization detector (FID) using an SM-6 column (6 m, 3 mm) and a gas chromatograph GC-2014 (Shimadzu Corp.) equipped with a flame ionization detector (FID) using a Xylene Master column PRC 7791 (50 m, 0.32 mm).

### 3. Results and Discussion

#### 3.1 Catalyst Characterization

Figure 1 shows the XRD patterns of the H-ZSM-5 and P-HZSM-5 catalysts. The MFI structure of H-ZSM-5 was retained after the treatment with H$_3$PO$_4$. The XRD patterns of P-HZSM-5 did not contain a broad peak indicating an amorphous phase. However, the peak intensity of the XRD patterns decreased after the H$_3$PO$_4$ treatment, possibly due to partial blockage of HZSM-5 pores by excess H$_3$PO$_4$ molecules because the XRD peak intensity of P-HZSM-5 decreased with higher contents of H$_3$PO$_4$ and recovered after removal of the excess H$_3$PO$_4$ by washing.

The molar ratios of P/Si and Si/Al in H-ZSM-5 and P-HZSM-5 catalysts were determined by Energy Dispersive X-ray Spectrometry (EDX) analysis. The acidic strength of the samples was analyzed by temperature-programmed desorption of ammonia (NH$_3$-TPD) using an Autosorb-1-Chemi (Quantachrome Instruments) in the temperature range from 373 to 973 K. A 0.2 g sample was pretreated in helium at 773 K for 1 h, then cooled to 373 K for 1 h. After NH$_3$ was adsorbed on the samples for 2 h, temperature-programmed desorption was started at 10 K/min from 373 to 973 K using a Quantachrome TPRWin v2.0.
tions in the aqueous solutions. The remaining phosphorus species after the washing must be strongly adsorbed by interacting with the pore surface of H-ZSM-5 zeolite.

The Si/Al ratios were increased after washing. The Si/Al molar ratios increased with higher concentration of H₃PO₄ in the solution, which might be caused by partial dealumination over H-ZSM-5 by the H₃PO₄ treatment. For the 5.5P-Z samples, more than half of the Al was dissolved from the H-ZSM-5 framework.

The models for H₃PO₄ deposited on the external surface and inside the pore before and after calcination were previously described19). Various interactions of phosphorus with the Brönsted acid sites of H-ZSM-5 prepared by impregnation with H₃PO₄ and calcinations have been proposed by some researchers20)~23). The models proposed by Kaeding et al.21) and Lercher et al.22) are illustrated in Figs. 3(a) and (b), respectively. Recently, a schematic mechanism for the phosphorus interaction with H-ZSM-5 was suggested as shown in Fig. 3(c)17). Two zeolitic hydroxyls are condensed with one phosphate molecule after calcination in air leading to a decrease in the number of OH groups on P modification. This mechanism has been convincingly supported by D₂/OH measurements.

Figure 4 shows the NH₃-TPD profiles of H-ZSM-5 and P-HZSM-5. There are two desorption peaks for H-ZSM-5, one in the range of 373-473 K and the other from 523 to 723 K, corresponding to the weak acid sites and strong acid sites, respectively. The peak intensity for the strong acid sites decreased with higher H₃PO₄ content whereas the desorption peak for weak acid sites was not changed so much. After washing with deionized water, the peak for strong acid sites slightly reappeared. These new acid sites might be caused by the interaction of phosphorus with the Brönsted acid sites of H-ZSM-5 as shown in Fig. 3.

3.2. MTO Reactions over H-ZSM-5 and P-HZSM-5

The methanol conversions and product selectivities over various catalysts are listed in Table 2. The product selectivities were calculated based on the total amount of the products, including aromatic compounds. With increasing H₃PO₄ content, the selectivities for ethylene and aromatics were decreased and the propylene selectivity was increased. The highest propylene selectivity obtained in this study was about 57%, which is very high compared to the reported values. Ethylene was formed predominantly via aromatics such as xylene and/or trimethylbenzenes12). The hydrogen transfer reactions take place on strong acid sites. Apparently, the formation of aromatics and ethylene was inhibited by the decrease in the numbers of strong acid sites after the H₃PO₄ treatment.

The selectivity for propylene reached 54.9% over 3P-Z catalyst. However, by increasing the H₃PO₄ content further, the methanol conversion over 5.5P-Z decreased to 71.1% and light olefin selectivity was about 3%. Instead, dimethylether (DME) was a main product. After the removal of excess H₃PO₄ by washing, the selectivity for ethylene and aromatics as well as propylene was increased again due to the partial recovery of strong acid sites. However, the acidity of the strong acid sites was still lower than that on the untreated H-ZSM-5 due to the partial dealumination.

Figures 5-10 show the changes in methanol conversions and product selectivities with reaction time. The
selectivities for hydrocarbons were calculated from the product amounts excluding aromatic compounds. The selectivity for propylene over the 3P-Z catalyst was slightly decreased after several hours with the presence of DME. The selectivity for DME was slightly increased after 200 min, indicating that catalytic deactivation by coke formation occurred over the catalyst with high phosphorus contents. Catalytic deactivation was obviously observed over the 4.5P-Z and 5.5P-Z catalysts (Figs. 9 and 10). After the deactivation, DME was mainly produced. DME is formed by methanol dehydration, which is the first step of the MTO reactions. The strong acid sites must have been covered with excess H₃PO₄ molecules which inhibited the conversion of DME into other hydrocarbons. In addition, for the samples before washing (4.5P-Z and 5.5P-Z), octahedral aluminum species must have remained inside the pores as a result of dealumination in the H₃PO₄ solutions with high concentrations. These aluminum species would reduce the durability in the MTO reaction.

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The methanol conversions and propylene selectivities were much improved after washing. The catalyst performance of W4.5P-Z and W5.5P-Z was very stable with very high propylene selectivities because the acidity of the strong acid sites of H-ZSM-5 after dealumination was lower than that of untreated H-ZSM-5.

The effect of W/F on the product selectivities is shown in Fig. 11. The reactions were performed over

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**Table 2 Methanol Conversion and Product Selectivity over H-ZSM-5 and P-HZSM-5 Catalysts**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion [%]</th>
<th>C₁</th>
<th>C₂⁺</th>
<th>C₃⁻</th>
<th>C₄⁺</th>
<th>C₅⁻</th>
<th>DME</th>
<th>Aromatics</th>
</tr>
</thead>
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<tr>
<td>H-ZSM-5</td>
<td>100</td>
<td>1.5</td>
<td>22.5</td>
<td>3.1</td>
<td>39.0</td>
<td>3.7</td>
<td>13.4</td>
<td>5.8</td>
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<tr>
<td>1P-Z</td>
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<td>1.7</td>
<td>19.9</td>
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<td>41.1</td>
<td>3.3</td>
<td>16.4</td>
<td>7.9</td>
</tr>
<tr>
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<td>1.9</td>
<td>17.4</td>
<td>1.3</td>
<td>48.4</td>
<td>2.1</td>
<td>18.0</td>
<td>8.2</td>
</tr>
<tr>
<td>3P-Z</td>
<td>100</td>
<td>1.9</td>
<td>8.9</td>
<td>0.7</td>
<td>54.9</td>
<td>1.6</td>
<td>17.10</td>
<td>13.9</td>
</tr>
<tr>
<td>4.5P-Z</td>
<td>86.8</td>
<td>4.8</td>
<td>6.8</td>
<td>0.4</td>
<td>52.6</td>
<td>0.7</td>
<td>18.3</td>
<td>14.7</td>
</tr>
<tr>
<td>5.5P-Z</td>
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<td>1.3</td>
<td>2.3</td>
<td>0.4</td>
<td>5.0</td>
<td>0.3</td>
<td>0.3</td>
<td>94.5</td>
</tr>
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<td>22.0</td>
<td>3.8</td>
<td>37.3</td>
<td>5.2</td>
<td>14.7</td>
<td>7.6</td>
</tr>
<tr>
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<td>22.6</td>
<td>3.3</td>
<td>40.7</td>
<td>4.3</td>
<td>15.1</td>
<td>7.0</td>
</tr>
<tr>
<td>W3P-Z</td>
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<td>1.5</td>
<td>19.9</td>
<td>2.4</td>
<td>45.7</td>
<td>2.8</td>
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</tr>
<tr>
<td>W4.5P-Z</td>
<td>100</td>
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<td>9.6</td>
<td>0.6</td>
<td>57.0</td>
<td>1.0</td>
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<tr>
<td>W5.5P-Z</td>
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<td>0.4</td>
<td>52.9</td>
<td>0.9</td>
<td>16.2</td>
<td>14.4</td>
</tr>
</tbody>
</table>

W/F = 0.065 kg·h⁻¹·mol⁻¹, reaction temperature = 723 K, reaction time = 30 min.

**Fig. 5 Methanol Conversion and Product Selectivities over H-ZSM-5 at 723 K**

**Fig. 6 Methanol Conversion and Product Selectivities over (a): 1P-Z; (b): W1P-Z at 723 K**
the 3P-Z catalyst at 723 K. The data were collected after reaction for 30 min. The selectivities for hydrocarbons were calculated based on the amount of products excluding aromatic compounds. The conversion of methanol was 100% for each W/F. However, a small fraction of DME was formed at a low W/F of 0.024 kg·h·mol⁻¹, indicating that the contact time was not sufficient to convert all DME to olefins. The highest selectivities for propylene were obtained at W/F from 0.033 to 0.065 kg·h·mol⁻¹.

The effects of reaction temperature on methanol conversion and product selectivity are shown in Fig. 12. The reactions were carried out at W/F = 0.065 kg·h·mol⁻¹ over the 3P-Z catalyst. The methanol conversion was nearly 80% at 573 K, whereas the main product was DME with other hydrocarbons as minor products. On the other hand, MTO reaction over untreated H-ZSM-5 showed nearly 100% methanol conversion with a small amount of DME at 573 K. These results indicate that the acidity was weakened by the H₃PO₄ treatment, suggesting that higher temperatures are required for MTO reactions over P-HZSM-5 catalysts. The highest selectivity for propylene (nearly 57%) was obtained at 723 K, although the selectivity for aromatics was not significantly increased at other temperatures.

4. Conclusions

H-ZSM-5 catalyst was treated with H₃PO₄ solutions of various concentrations. The selectivities for olefins over P-ZSM-5 in the MTO reactions were significantly improved by the H₃PO₄ treatment. Higher phosphorus content in P-HZSM-5 significantly decreased the selectivity for ethylene and aromatics due to lower acidity of the strong acid sites of H-ZSM-5 caused by de-alumination. The highest selectivity for propylene over modified P-HZSM-5 reached 57% with small amounts of aromatic by-products. The removal of excess H₃PO₄ after washing resulted in partial recovery of the strong acid sites. The catalyst performance of washed P-HZSM-5 was very stable with very high propylene selectivities.

The significant increase in propylene selectivity over P-HZSM-5 catalysts has important practical applications in current petroleum chemistry.

Acknowledgment

The authors wish to thank Prof. T. Hirai, Dr. Y. Shiraishi, Dr. M. Morishita and Mr. K. Murata at Osaka University for NH$_3$-TPD measurements.

Fig. 9  Methanol Conversion and Product Selectivities over (a): 4.5P-Z; (b): W4.5P-Z at 723 K

W/F = 0.065 kg·h·mol$^{-1}$.

Fig. 10  Methanol Conversion and Product Selectivities over (a): 5.5P-Z; (b): W5.5P-Z at 723 K

W/F = 0.065 kg·h·mol$^{-1}$.

Fig. 11  Product Selectivities over 3P-Z Catalyst at 723 K

W/F: (a) 0.024; (b) 0.033; (c) 0.065; (d) 0.200 kg·h·mol$^{-1}$.

Reaction time of 30 min.

Fig. 12  Effect of Temperature on Methanol Conversion and Product Selectivities over H-ZSM-5 and 3P-Z Catalysts in MTO Reaction at W/F of 0.065 kg·h·mol$^{-1}$

Reaction time of 30 min. Methanol conversions are 100% (H-ZSM-5, 573 K), 79.1% (3P-Z, 573 K), 100% (3P-Z, 673 K) and 100% (3P-Z, 773 K).
References


要 旨
リン酸処理した H-ZSM-5 触媒を用いたプロピレン高選択性による Methanol-to-olefin 反応

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H-ZSM-5ゼオライトを種々の濃度のリン酸水溶液に浸漬し乾燥させたリン酸修飾 H-ZSM-5 (P-HZSM-5), およびこれを水で洗浄した触媒を調製した。生成物のP/Al および Si/AlをEDXにて測定した。H-ZSM-5のSi/Al比は、リン酸水溶液の濃度の増加とともに増加したことから、リン酸修飾による脱アルミングが起こったものと考えられる。洗浄後もリン酸水溶液の濃度の増加とともに増加した。リン酸処理は ZSM-5細孔表面に強い相互作用を結びついているものと思われる。本触媒を methanol-to-olefin 反応に用いたところ、メタノールの転化率100％の条件で、5％以上の高いプロピレン選択性を示した。同時に、触媒の安定性も向上した。アンモニア TPD 測定により、H-ZSM-5の強酸点の酸量がリン酸処理によって減少することが分かった。その結果、芳香族炭化水素およびコーキの生成が抑制され、高い低級オレフィン選択性および触媒の優れた安定性が得られたものと思われる。